



Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879



A Short Review on SPEEK-Based Direct Methanol Fuel Cell (DMFC) for Automotive Power Systems

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ARTICLE INFO

Article history:

Received 26 August 2019

Received in revised form 19 November 2019

Accepted 22 November 2019

Available online 30 December 2019

Keywords:

Direct methanol fuel cell (DMFC);
Sulfonated Poly (Ether Ether Ketone)
(SPEEK); automotive industries

ABSTRACT

This review paper is to explain the current technology of SPEEK-based direct methanol fuel cell (DMFC) for automotive power systems. These green technology devices have received worldwide recognition and the product prototype was successfully tested in house. The primary objective of the review is to explain the production of SPEEK-based DMFC for automotive power systems, replacing a petrol and diesel used in a currently commercialize car fuel. The other objective is to produce SPEEK-based DMFC which has been proven via lab scale analysis to have better performance than commercially available Nafion® membrane for DMFC. The SPEEK-DMFC is a noiseless, environmentally friendly device and possess longer lifetime compare to the available petrol or diesel currently available in petrol station.

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1. Introduction

Development and utilization of technologies for product innovation and new services are critical element of knowledge economy. Therefore, sharing and exchanging ideas among institutions could lead to new breakthrough for production of modern products. According to report by previous studies, it was advised that both funders and policymakers should constantly explore new areas for investment by highlighting most profitable field and recruit students in universities to study the particular area [1-2]. This technology transfer applied mostly in research institutions such as universities, aims to improve the public goods and creates new businesses and employment opportunities. Lesson learnt from Malaysia economic crisis in year 1997-1998 is not to rely on direct investments by foreign countries for the development of economy [3-4], as they have the flexibility to withdraw their investment and shift to other profitable countries. In Malaysia, Small and Medium

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Enterprises (SME) has been introduced as a system for domestic investment and catalyse economic expansion where year 2016 reported a total of 98.5 % business establishments under SME. Services hold the major percentage of 89.2 %, followed by manufacturing 5.3 %, construction, agricultural and mining and quarrying.

Policy of SME Masterplan (2012-2020) can be summarised as evolution of economy by developing competitive and innovative technological sector that can compete with global competitors and thus achieving industrial country status or known as high-income country by 2020 [5-6]. Strategies are to put more efforts in manufacturing, agricultural and services field in order to increase the value chain. Also, the Government support the development by providing modules and programmes which can be breakdown into two categories; “Financial Assistance” and “Business Support Services” under various Ministries and Agencies. The fund under Commercialisation of Public Sector R & D (CRDF 1) is one of the types of several financial assistants given by the government and managed by Malaysian Technology Development Corporation (MTDC). Table 1 shows several resolutions established for development of SMEs.

Table 1
SMEs development’s resolution

Resolution	Description
Outsourcing	Related programmes will be introduced and conducted to cultivate SME as partners in product Research and Development. Three-way collaborations between Multinational Corporation, Government-linked companies and SME helps to promote technology transfer and development of skills and marketing.
Inter-relationship between firms	Business linkage between GLC, MNC and SME allows the SME to be more reliable and competitive for global supplier networks. This network can help to expand the nation’s trade with new trade markets.
Enterprise-related programmes	In order to enhance SMEs management and business skills, operation techniques, quality enhancement and marketing skills, programmes such as advisory and outreach services would be expanded.
Knowledge skills	Develop and improve technical expertise of SMEs companies to generate innovative product and establishing new financial value via knowledge application.

2. DMFC Configurations

Figure 1 shows the design of SPEEK-based DMFC and Figure 2 shows the operation of DMFC system. The system can be divided into 3 main components; DMFC stack, DMFC system and DC-AC alternator. The heart of the DMFC stack is our in-house SPEEK-based membrane, which has been proven via lab scale analysis to have better performance than commercially available Nafion® membrane [7]. To produce sufficient electricity for the consumer, 60 DMFC cells are stacked together to form a single DMFC stack that can generate 36 V and 30 A of electricity. To produce the electricity, methanol fuel solution with 1-2 M concentration is feed to the anodic side of the DMFC stack via a pump. Air is fed using a blower to the cathode side of the DMFC stack. Electrochemical reaction between methanol solution and air will generate free electron that can be used to do electrical work. Excess fuel from the stack will flow back to tank. The electricity generated from the DMFC system is used to power-up a DC motor which is tied to an alternator to produce 230 V, AC current electricity [8]. Figure 3 summarized the operation of the DMFC.

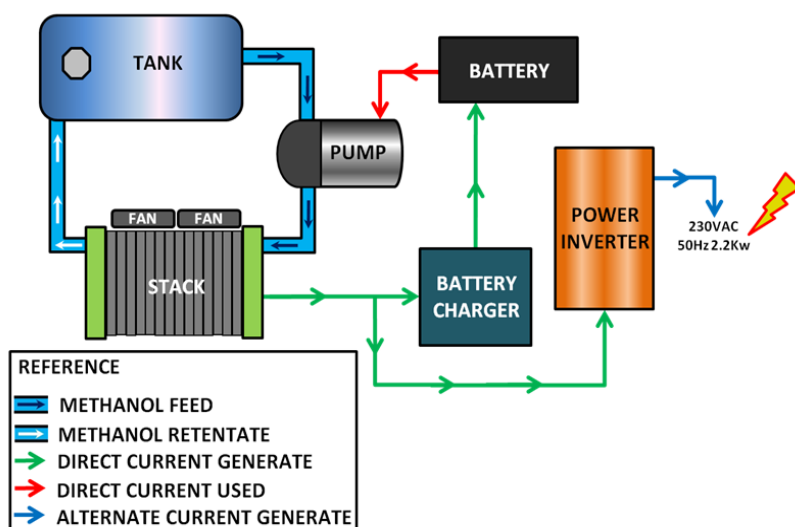


Fig. 1. Design of SPEEK-based DMFC

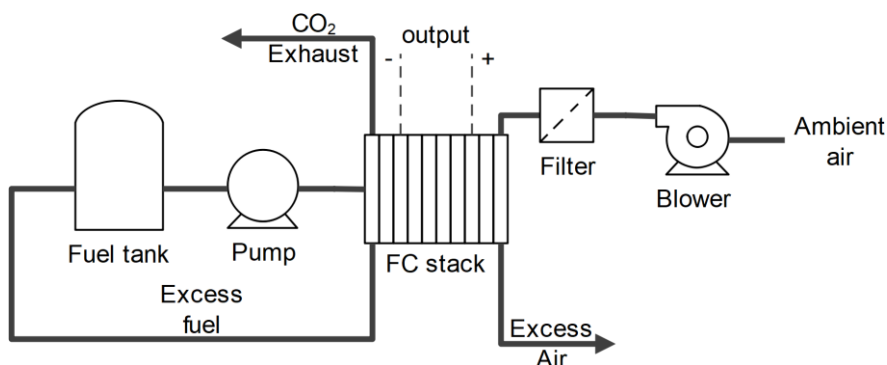


Fig. 2. Illustration for DMFC operation

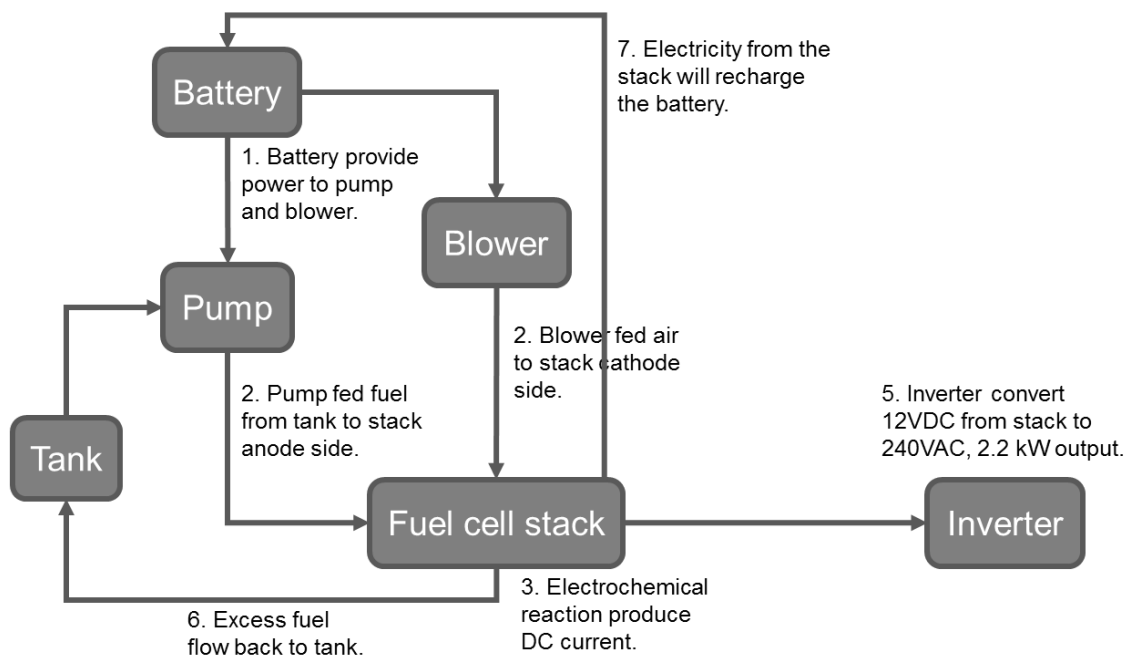


Fig. 3. Summary of SPEEK-based DMFC

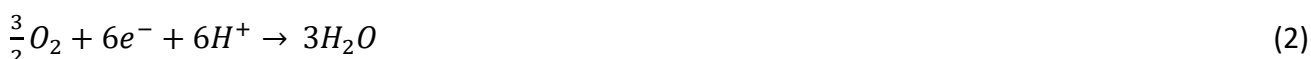
3. Direct Methanol Fuel Cell (DMFC)

There are many types of fuel cell but increasingly popular type of fuel cell nowadays is known as direct methanol fuel cell (DMFC). Fuel cell can be defined as an electrochemical device which transforms free energy from redox processes directly to electrical energy, dissipating heat as the by-product [9]. In DMFC operation, aqueous methanol diffuses from diffusion layer to catalytic layer, in which it would electrochemically oxidize into three; protons, electrons and carbon dioxide. Protons from the reaction diffuses through electrolyte membrane to cathodic side and next, reacting with oxygen from air inside the catalytic layer to form water [10]. Following equation depicts reaction that occurs at cathode and anode side of the DMFC.

Anodic side reaction



Cathodic side reaction



Overall reaction



It is beneficial to replace conventional energy production to fuel cell technology as future energy generation [5, 11]. Since fuel cell generates electricity directly from the chemical reaction using electrochemical principle, the energy loss due to heat production is lower than the conventional energy production technology, which can increase the fuel cell energy conversion efficiency. Previous researcher stated in their book (Fuel Cell Fundamentals) that the fuel cell efficiency is around 60 %, which is higher than any conventional energy production, which has efficiency around 40 % only [12]. Higher energy conversion efficiency means that the fuel cell needs less fuel to produce similar energy output as generated by the existing energy production technology. Therefore, the fuel cell will produce less greenhouse gas by-products as compared to the established energy production technology. This can reduce the carbon footprint issue [13]. Other than that, fuel cell system is simple since the fuel cell only needs anode and cathode electrode layer, and an electrolyte to produce electricity [14]. Therefore, the fuel cell can be scaled up or scaled down according to the energy requirement, whereby the fuel cell does not experience energy losses issue when scaling down to smaller size as compared to gas turbines or reciprocating engines [15]. Last but not least, methanol fuel is cheap, easier to handle than H₂ fuel at room temperature, and has a higher volumetric energy density (3,800 kcal/L) compare to H₂ fuel (658 kcal/L) [16]. Based on these advantages, DMFC has good potential to be commercialized as the next generation energy production technology in the future [17].

3.1 Sulfonated Poly (Ether Ether Ketone) (SPEEK) Nanocomposite Membrane

Proton exchange membrane, or also known as polymer electrolyte membrane (PEM) is the main component in DMFC operation [18]. Its function is similar to salt bridge in galvanic cells that connects the half-cell of anode and cathode, and permits protons to move from anode to cathode. Simultaneously, PEM blocks the current from electrons and prevent the mixing of reactant and fuel which keeps the electrodes separated throughout the process. Prime features of PEM in DMFC process is having high proton conductivity and low methanol permeance. These characteristics enable the process to result in high performance and high-power output. At the same time, to have a good operational lifespan, the PEM also need to have good stability and high resistance towards harsh environments in DMFC operation [19]. Last but not least, the PEM should be able to sustain sufficient hydration to allow transfer of protons between anode and cathode but not excessively to maintain good contacts between electrodes and PEM [20]. Perfluorosulfonic acid (PFSA) is widely utilized as PEM in DMFC operation due to its advantages such as superior performance and excellent stability in polymer electrolyte membrane fuel cell (PEMFC) operation [21]. However, the PFSA membrane has low methanol barrier properties which could drop the DMFC efficiency up to 35 % [13]. Other than that, the cost to produce the PFSA membrane is too high and causes the overall DMFC cost unappealing for mass production. Therefore, many attempts have been made to develop the new type of PEM with good stability, comparable performance and cheaper than PFSA membrane for DMFC operation. Membrane based from SPEEK is identified to be potential alternative in developing high performance PEM for DMFC operation. Similar to PFSA, SPEEK also possess high chemical and thermal stability which makes it suitable for the process [8]. However, our previous study discovered that proton conductivity of SPEEK membrane (2.71×10^{-2} S/cm) was doubled compared to PFSA membrane (1.35×10^{-2} S/cm). Moreover, the methanol permeation value of the SPEEK membrane was 87 % lower than the PFSA membrane (7.59×10^{-7} cm²/s and 63.0×10^{-7} cm²/s for SPEEK and PFSA membrane, respectively). Thus, from the aforementioned results, it can be assumed that PEM using SPEEK membrane could improve the power output and efficiency of the DMFC system [7].

Even though the SPEEK membrane has shown better performance than the PFSA membrane, the SPEEK membrane tends to absorb more water as compared to the PFSA membrane [22]. This characteristic affects the stability of the SPEEK membrane and could jeopardize the DMFC lifespan [7]. In order to overcome the limitation, inorganic nanoparticles were embedded into the composite membrane to increase the stability and eventually enhance the performance when compared to pristine membrane [7]. According to a study, incorporation of inorganic montmorillonite (MMT) particles and 2,4,6-Pyrimidinetriamine (TAP) compatibilizer, SPEEK/MMT/TAP resulted in 52 % lower water uptake than pristine SPEEK membrane [8]. Proton conductivity and methanol permeability performance was enhanced due to presence of MMT nanoparticles. SPEEK/MMT/TAP membrane also resulted in higher energy output compared to pristine SPEEK and PFSA membrane during series of performance tests. Therefore, implementation of SPEEK/MMT/TAP nanocomposite membrane for development high-performance and high efficiency DMFC prototype is considered.

3.2 Product Manufacturing

Figure 4 shows product manufacturing flow chart.

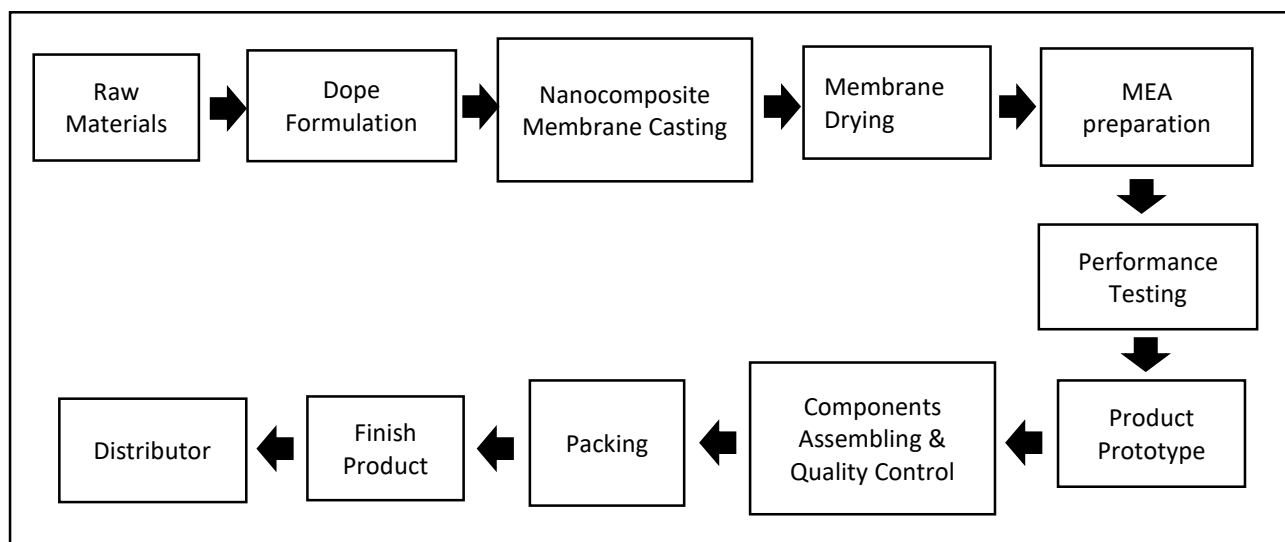


Fig. 4. Product manufacturing flow chart

3.2.1 Membrane electrode assembly production

Membrane electrode assembly production (MEA) are membrane layers that were coated with catalyst and it is where the chemical reaction occurs. Manufacturing of MEA can be done by hot pressing anode and cathode to the membrane at operating condition of 80°C and at pressure 80 kg/cm² for 2 minutes. MEA surface area for reaction was found to be 6.0 cm². Cathode side consist of PtRu-supported carbon catalyst with binder Nafion DE1021CS (Binder/Carbon=1) while the anode side consist of PtRu-supported carbon catalyst with binder Nafion DE1021CS (Binder/Carbon=0.75).

3.2.2 Graphite plate fabrication

Excellent mechanical strength, high resistance to chemical and high conductivity graphite plate was purchased from the supplier. The plate was sent for cutting and milling based on design in Figure 5. The grooves for anode and cathode sides were fabricated to allow sufficient and uniform reactant (methanol and air) supply to MEA active site and transport by-product compound (carbon dioxide and water) from the system. Table 2 shows graphite plate specifications while Figure 5 shows graphite plate design for anode (top) and cathode (bottom) sides.

Table 2

Graphite plate specifications

Plate Physical Properties	
Plate Grade	Fuel Cell Grade (FU 4369)
Bulk Density	1.90 g/cm
Hardness	>100 (Rockwell (HRB 10/40))
Compressive Strength	>50 MPa or 7250 psi
Flexural Strength	>40 MPa or 6090 psi
Young's Modulus – Flexural	10 GPa or 1.45×10^6
Young's Modulus – Dynamic	24 GPa or 3.48×10^6
Plate Electrical Properties	
Specific Electrical Conductivity – XY (In-Plane)	110 S/cm
Specific Electrical Conductivity – Z (Through-Plane)	20 S/cm
Specific Electrical Resistance – XY (In-Plane)	90 $\mu\Omega$ /M
Specific Electrical Resistance – Z (Through-Plane)	190 $\mu\Omega$ /M (DIN 51 911) 500 $\mu\Omega$ /M (Internal Specification)
Long Term Stability	
Various Acids at 85°C and 180°C (185F and 356F)	2000 h
Mineral Oil at 85°C and 185°C (185F and 356F)	2000 h
Methanol at 90°C (194F)	3000 h
Other Plate Properties	
Thermal Conductivity	55 W/mK

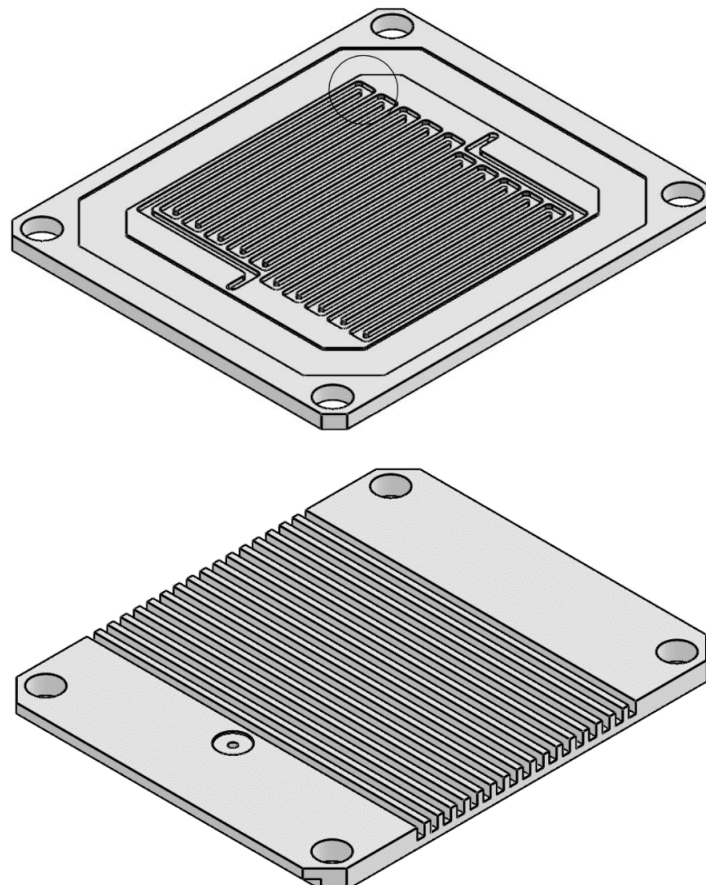


Fig. 5. Graphite plate design for anode (top) and cathode (bottom) sides

4. DMFC Evolution

DMFC was first employed and invented by researchers from various institutions located in United States, which includes NASA and Jet Propulsion Laboratory during the 1990s. It was introduced as a new fuelcell-based technology. Green, renewable technology with high performance efficiency are very scarce and challenging even in current modern era. It is still in research and development phases. This technology targeted to supply energy for electronic devices industry and also larger power generation industry such as in remote area or for micro-distributors. Particularly, DMFC are improvisation from hydrogen PEMFC, which have high potential for application in electronic and transportation sectors as it is a liquid-typed fuel [20]. Smaller energy application such as in mobile phones, laptop to medium-energy application such as in medical devices and weather stations could also utilized DMFC as its power sources. Studies done by researchers also suggested that DMFC is the most promising candidate for rechargeable battery technology. However, few limitations need to be addressed before the technology can be proceed for commercialization. Currently, researches on fuel cell technology are mostly focusing on application of DMFC due to its beneficial characteristics.

Despite having greater energy density which is around five to ten times higher compared to rechargeable batteries, DMFC can be operated for longer time with lower cost than other existing batteries. However, the pricing of micro fuel cell components is still in polemics. Putting the issue aside, DMFC technology are readily applicable for real life application and utilization of DMFC as power sources can helps to improve the environment for future mankind. The development of this viable technology in Malaysia is crucially important because of the many advantages offered by membrane for the various industries. As a result, Malaysia will be one of the most important countries in the next decade that is able to develop this technology through the expertise developed by numerous researchers. Energy is one of the most precious commodities in our modern world. Population expansion and technology advancement are two main reason to the increment of energy demand. Based on *Malaysia Energy Statistics 2016* published by *Malaysia Energy Commission* (Figure 6), energy demands in Malaysia increased 56 % from 1994 to 2014.

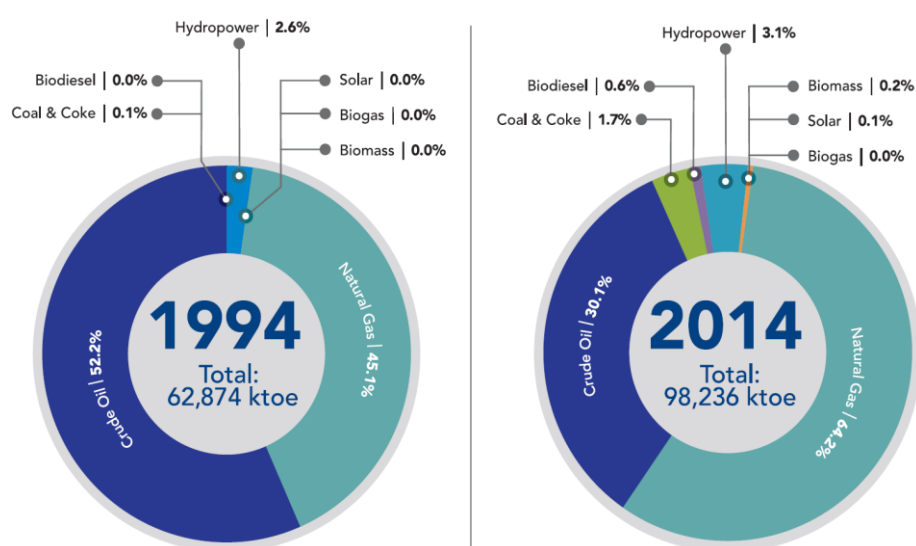


Fig. 6. Malaysia Energy Statistics charts

Interestingly, at the same time, our dependency for energy from fossil fuel has reduced by 1.4 %. The statistics shows that Malaysia's government is committed to reduce Malaysia's carbon footprint and increase market share for green and renewable energy, in accordance with the *National Renewable Energy Policy and Action Plan 2009*, *Renewable Energy Act 2011* and *Sustainable Energy*

Development Authority Act 2011. Therefore, clean energy product based on DMFC technology has potential for commercialization in today's Malaysia market.

4.1 DMFC Market Size

DMFC in 2016 achieved market value of 18.57 billion USD and the value is expected to reach 24.25 billion USD by 2021. The report also stated that Asia Pacific market will be dominating worldwide sales market as a result from manufacturing sector development, IT industry and healthcare infrastructure. Currently, most of DMFC product is still under development or funded by government for military purposes. Only two companies have already launched their DMFC product to market, which are Oorja Corporation and SFC Energy (Figure 7).



Fig. 7. Other products based on DMFC technology

Oorja Corporation produced modular DMFCs ranging in power from 1 to 5 kW. Their products have been used for various application including wireless telecommunication, materials handling industries, and backup power. The company is based in California. The product of SFC Energy was called as EFOY fuel cells. These products can be used in caravan, chalet or on board a boat to automatically recharge batteries and available for usage anytime, in which the term 'mobile power socket' fits the situation. Whereas, for the industrial users, this EFOY fuel cell can provide off-grid power wherever and whenever needed, no matter at what weather to transferring the data. This company was based at Deutschland.

5. Conclusions

DMFC development takes their consumers into new green technology power efficient era and transform the conventional fossil-based fuel source into more environmentally friendly fuel cell. It promises higher power performance, longer fuel consumption, and minimal CO₂ emission yield [23-25]. The main focus in this review is to compute detail formulated fuel cell membrane with the capacity of converting diluted methanol into electron charges that provide electricity for any application. Complied with its ability, the aim is to substitute current carbon-based fuel into

environmentally sustainable fuel cell membrane and ensure our mother earth free from further contamination from prolonged use of combustion of fossil fuel.

Acknowledgement

Authors would like to extend their gratitude to Ministry of Higher Education Malaysia and Universiti Malaysia Pahang (UMP) with grant number RDU192615.

References

- [1] Dixon, R. K., J. Li, and M. Q. Wang. "Progress in hydrogen energy infrastructure development—addressing technical and institutional barriers." In *Compendium of Hydrogen Energy*, pp. 323-343. Woodhead Publishing, 2016.
- [2] Abedini, Reza, and Amir Nezhadmoghadam. "Application of membrane in gas separation processes: its suitability and mechanisms." *Petroleum & Coal* 52, no. 2 (2010): 69-80.
- [3] Sazali, Norazlian, Wan Norharyati Wan Salleh, Ahmad Fauzi Ismail, Kumaran Kadirgama, Mohamad Shahrizan Moslan, Faten Ermala Che Othman, Nor Hafiza Ismail, Mahendran Samykano, and Zawati Harun. "Effect of heating rates on the microstructure and gas permeation properties of carbon membranes." *Malaysian Journal of Fundamental and Applied Sciences* 14, no. 3 (2018): 378-381.
- [4] Ismail, N. H., W. N. W. Salleh, N. Sazali, M. A. Mohamed, N. Rosman, and N. Yusof. "EFFECT OF P84 (BTDA-TDI/MDI) COMPOSITION TOWARDS THE PERFORMANCE OF THE DISK SUPPORTED CARBON MEMBRANE." *Jurnal Teknologi* 79, no. 1-2 (2017).
- [5] Ajanovic, Amela, and Reinhard Haas. "Economic prospects and policy framework for hydrogen as fuel in the transport sector." *Energy policy* 123 (2018): 280-288.
- [6] Ummartyotin, S., and C. Pechyen. "Strategies for development and implementation of bio-based materials as effective renewable resources of energy: A comprehensive review on adsorbent technology." *Renewable and Sustainable Energy Reviews* 62 (2016): 654-664.
- [7] Jaafar, Juhana, A. F. Ismail, T. Matsuura, and Kazukiyo Nagai. "Performance of SPEEK based polymer–nanoclay inorganic membrane for DMFC." *Journal of membrane science* 382, no. 1-2 (2011): 202-211.
- [8] Salleh, Muhammad Taufiq, Juhana Jaafar, Mohamad Azuwa Mohamed, M. N. A. M. Norddin, A. F. Ismail, M. H. D. Othman, Mukhlis A. Rahman, N. Yusof, F. Aziz, and W. N. W. Salleh. "Stability of SPEEK/Cloisite®/TAP nanocomposite membrane under Fenton reagent condition for direct methanol fuel cell application." *Polymer Degradation and Stability* 137 (2017): 83-99.
- [9] Ilbeygi, Hamid, Mostafa Ghasemi, D. Emadzadeh, Ahmad Fauzi Ismail, S. M. J. Zaidi, Saad A. Aljlil, Juhana Jaafar, Darren Martin, and Samaneh Keshani. "Power generation and wastewater treatment using a novel SPEEK nanocomposite membrane in a dual chamber microbial fuel cell." *International Journal of Hydrogen Energy* 40, no. 1 (2015): 477-487.
- [10] Choi, Seung-Hak, Mohammad S. Qahtani, and Eyad A. Qasem. "Multilayer thin-film composite membranes for helium enrichment." *Journal of membrane science* 553 (2018): 180-188.
- [11] Acar, Canan, and Ibrahim Dincer. "The potential role of hydrogen as a sustainable transportation fuel to combat global warming." *International Journal of Hydrogen Energy* (2018).
- [12] Muradov, N. "Emission-free fuel reformers for mobile and portable fuel cell applications." *Journal of power Sources* 118, no. 1-2 (2003): 320-324.
- [13] Collier, Amanda, Haijiang Wang, Xiao Zi Yuan, Jiuju Zhang, and David P. Wilkinson. "Degradation of polymer electrolyte membranes." *International Journal of Hydrogen Energy* 31, no. 13 (2006): 1838-1854.
- [14] Li, Hongtao, Gang Zhang, Jing Wu, Chengji Zhao, Qiong Jia, Christopher M. Lew, Liyuan Zhang et al. "A facile approach to prepare self-cross-linkable sulfonated poly (ether ether ketone) membranes for direct methanol fuel cells." *Journal of Power Sources* 195, no. 24 (2010): 8061-8066.
- [15] Sridhar, S., B. Smitha, and Apsar Shaik. "Pervaporation-Based Separation of Methanol/MTBE Mixtures—A Review." *Separation and Purification Reviews* 34, no. 1 (2005): 1-33.
- [16] Lei, Fengling, Zhongshui Li, Lingting Ye, Yanli Wang, and Shen Lin. "One-pot synthesis of Pt/SnO₂/GNs and its electro-photo-synergistic catalysis for methanol oxidation." *International Journal of Hydrogen Energy* 41, no. 1 (2016): 255-264.
- [17] Schemme, Steffen, Janos Lucian Breuer, Remzi Can Samsun, Ralf Peters, and Detlef Stolten. "Promising catalytic synthesis pathways towards higher alcohols as suitable transport fuels based on H₂ and CO₂." *Journal of CO₂ Utilization* 27 (2018): 223-237.

- [18] Wu, Zhen, Zaoxiao Zhang, and Meng Ni. "Modeling of a novel SOFC-PEMFC hybrid system coupled with thermal swing adsorption for H₂ purification: Parametric and exergy analyses." *Energy conversion and management* 174 (2018): 802-813.
- [19] Castel, Christophe, Lei Wang, Jean Pierre Corriou, and Eric Favre. "Steady vs unsteady membrane gas separation processes." *Chemical Engineering Science* 183 (2018): 136-147.
- [20] Hao, Jinkai, Yongyi Jiang, Xueqiang Gao, Feng Xie, Zhigang Shao, and Baolian Yi. "Degradation reduction of polybenzimidazole membrane blended with CeO₂ as a regenerative free radical scavenger." *Journal of Membrane Science* 522 (2017): 23-30.
- [21] Kim, Deuk Ju, Min Jae Jo, and Sang Yong Nam. "A review of polymer–nanocomposite electrolyte membranes for fuel cell application." *Journal of Industrial and Engineering Chemistry* 21 (2015): 36-52.
- [22] Pakizeh, Majid, S. A. A. Mansoori, Mahdi Pourafshari Chenar, and Mahdiah Namvar-Mahboub. "Modification of PSf membrane nanostructure using different fabrication parameters and investigation of the CO₂ separation properties of PDMS-coated PSf composite membranes." *Brazilian Journal of Chemical Engineering* 30, no. 2 (2013): 345-354.
- [23] Sazali, Norazlian, Wan Norharyati Wan Salleh, Ahmad Fauzi Ismail, Nor Hafiza Ismail, and Kumaran Kadirgama. "A brief review on carbon selective membranes from polymer blends for gas separation performance." *Reviews in Chemical Engineering*.
- [24] Sazali, N., W. N. W. Salleh, M. Nur Izwanne, Z. Harun, and K. Kadirgama. "Precursor Selection for Carbon Membrane Fabrication: A Review." *Journal of Applied Membrane Science & Technology* 22, no. 2 (2018).
- [25] Sazali, N., W. N. W. Salleh, NAH Md Nordin, and A. F. Ismail. "Matrimid-based carbon tubular membrane: Effect of carbonization environment." *Journal of Industrial and Engineering Chemistry* 32 (2015): 167-171.